

Mechanical and Chemical Characterizations of Polyester Modified Cement Immobilizing Nuclear Wastes

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Abstract

Improvement of the properties of cement waste forms-styrenated polyester based on poly (oxy-diethylene maleate) as a polymer additive was investigated. The composite material of cement/polymer was used as a matrix for the immobilization of borate waste simulates. Porosity and pore size distribution of the composite material and its final waste form were determined. The effect of water/cement ratio on the properties of obtained waste forms was studied using X-ray, mechanical and leaching measurements. The obtained results showed that the proposed matrix could be nominated as a suitable matrix to meet the anticipated requirements for long-term disposal.

Keywords

Cement Waste Form; Polyester Modified Cement; Nuclear Waste; Mechanical and Chemical Properties; Cs-137

Introduction

Cement materials have been used on a large scale as immobilization matrices for solidification/stabilization of radioactive wastes. Among the disadvantages of cement-waste forms is the pronounced high porosity, which in aqueous medium leads to return of radionuclides from the waste materials to the environments.

Polymer modified cement materials (Ohama, 1997, Kardon, 1997, Sumathy et al., 1997, and Amelina, et al., 1997) offer considerable improvement in properties and performance compared with traditional mortars (Salbin, 1997). Polymer cement composites using unsaturated polyester resins based on recycled poly(ethylene terephthalate) were investigated (Rebeiz, 1993) and are considered of importance for their potential applications in the nuclear field. The mechanism of interaction of polymers with the hydration products of Ordinary Portland Cement (OPC) has been also studied (Larbi and Bijen, 1990 and

Sugama and Kukacka, 1982).

In the present study, the effect of polymer on the hydration of (OPC) using different water/cement ratios have been studied based on porosity measurements, X-ray analysis, mechanical and chemical tests.

Experimental Approach

Materials and Solutions Used

1) Simulating waste solution

The chemical composition of the borate simulating waste solution used in the present study is given in table (1).

TABLE 1 CHEMICAL COMPOSITION OF SIMULATED BORATE WASTE SOLUTION CONCENTRATE (g/L)

NaOH	H ₃ BO ₃	Na ₂ SO ₄	Na ₂ HPO ₄ .12H ₂ O	NaCl	Fe ₂ (SO ₄) ₃
29	180	30	5	5	5

Although the chemical composition is basically the same, borate waste concentrates from pressurized water reactors vary slightly in their salt content according to the treatment process, conditions of reactor operation and coolant constituents. Waste material with relatively high borate concentration was chosen to simulate the worst possible composition that may affect negatively the immobilization process of waste varieties. Part of the prepared solution was labeled with a desired amount of carrier free radioactive cesium isotope. The spiked solution samples were immobilized in cement or in polymer modified cement and the obtained radioactive solidified waste forms were subjected to leach tests.

2) Cement Materials

The type of cement used in the current study is the Ordinary Portland Cement (OPC) manufactured according to British Standard Specifications (BSS) (British Standard Institution, 1969). The raw materials

were ground, sieved and a mesh size < 0.5 mm was chosen for this work. The chemical analysis of cement type used is given in table (2).

TABLE 2 THE CHEMICAL COMPOSITION OF ORDINARY PORTLAND CEMENT USED

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	SO ₃	Insoluble residues
19.84	4.74	4.0	61.01	2.5	0.6	2.4	0.95

- Lime saturation factor = 97% by weight.
- Loss on ignition = 3.5%.

3) Water Extended Polyester (PE)

Unsaturated polyester was prepared by heating maleic anhydride and diethylene glycol reacting under reflux at 190 °C for 4 hours. The unreacted monomer and other products were removed from the reaction mixture under vacuum and the acid number was adjusted at 50 mg of KOH/gm. Water extended polymer emulsions were prepared by dispersing water or waste solution samples containing 1.03% by weight triethanolamine as an emulsifier into the prepared unsaturated polyester containing 30% by weight styrene. The stable emulsion of polyester was cured by the addition of 2% by weight benzoyl peroxide (B.P.) as an initiator. More experimental details for the preparation of water extended polyester are given in previous publication (Ghattas, N.K. et al, 1988).

4) Leaching Solution

The ground water, used as leachant in the radionuclides release tests, is obtained from Abu-Zaabal well (Well No. 202) which is one of the nearest ground water well to Inshas reactor site where storage and disposal facilities for radioactive wastes have been constructed. The chemical composition of ground water used is represented in table (3).

TABLE 3 CONCENTRATION IN G/L OF SOME IONS OF INTEREST IN ABU-ZAABAL GROUND WATER

T.D.S. (g/L)	PH	Soluble cations (ppm)				Soluble anions (ppm)		
		K ⁺	Na ⁺	Mg ⁺⁺	Ca ⁺⁺	Cl ⁻	SO ₄ ⁻⁻	HCO ₃ ⁻
1.05	7.2	23	149	13	74	137	317	272

T.D.S. = Total dissolved salts.

Immobilization of Waste Solution Simulate

Spiked and unspiked waste solution simulates were thoroughly mixed with OPC (< 0.5 mm mesh size). Immobilization in polyester-modified cement (using different water/cement ratios) was performed by

mixing the required percentage of stable emulsion of styrenated polyester (30% wt. styrene, 70% wt. polyester and 2% wt. B.P.) with the cement paste. The homogenous, cement-waste mixtures or polymer premix cement-waste mixtures were poured into cylindrical molds and tightly closed for 28 days. Unspiked simulating waste solution samples were immobilized and the obtained solid cold blocks were used for physical, mechanical and porosity measurements. On the other hand, the spiked solutions were immobilized following the same techniques and the cured hot specimens were subjected to leaching tests.

Physical, Mechanical and Chemical Characteristics of Solidified Waste Forms

1) X-Ray Analysis

X-ray diffraction pattern of powdered specimens of plain cement and polymer-modified cement with and without 4% borate waste by wt. were examined using 1930 Philips type Diffractometer with CuK α radiation and Ni-filter.

2) Porosity

Porosity was studied using a Micrometrics, Pore Sizer 9310, the sample size was 15 cc, the max. applied pressure was 30000 PSI, the contact angle θ was 130° and a correction was made for mercury compressibility.

3) Mechanical Properties

Mechanical properties were studied by measuring the compressive strength of the solidified samples using Instron Universal Testing Instrument Mode 1178 (ASTM-D-695).

4) Chemical Properties

Chemical properties were followed by performing leaching tests using Ortiz-single channel analyzer.

Results and Discussions

Immobilization of borate waste in polymer modified cement matrices and transformation of the waste solution into monolithic homogenous solid aims at improving the final waste form and reducing the potential migration and dispersion of radionuclides from waste form to the environment. In the present study styrenated polyester based on poly(oxy diethylene maleate) was used to improve the cement waste form as previously stated.

Mechanical Properties

Mechanical integrity of the waste forms is an important consideration in the safe handling, transportation and disposal of radioactive waste. The interpretation of the experimental results and the durability of polymer modified cement waste forms are based on good understanding of the chemical interaction of polymer cement composition. X-ray diffraction, porosity, and mechanical analyses were performed for blocks having different water cement ratios. The compressive load required to cause failure for the cured final waste forms was determined for 5 – 6 cylindrical blocks having the dimensions of 6.0 ± 0.5 cm height and 3.1 ± 0.5 cm diameter. Compressive strength measurements for cement polymer modified cement and polymer modified-cement containing 4% by weight borate waste simulate were carried out using three different water/cement ratios ($w/c = 0.35, 0.40, 0.45$). The average compressive strength values measured for the prepared samples were represented in table (4). The data obtained for plain cement and the polymer modified cement show that increasing water/cement ratio from 0.35 to 0.4 decreased compressive strength values. This may be due to the increase in porosity of the solidified cement blocks having water/cement ratio higher than 0.35. The obtained results are supported by the previously published studies (Seishi and Della, 1981).

TABLE 4 COMPRESSIVE STRENGTH VALUES IN KG/CM² FOR PLAIN CEMENT, CEMENT-PE MODIFIED AND THE FINAL WASTE FORMS HAVING DIFFERENT WATER/CEMENT RATIOS

Water ratio	w/c = 0.35	w/c = 0.40	w/c = 0.45
Plain cement	241	217	221
2% by weight PE modified cement	265	245	247
2% by weight PE modified cement + 4% borate waste	250	212	153

It is worth mentioning that no significant differences in compressive strength values were observed during increasing water/cement ratio from 0.4 to 0.45 for borate free samples. It was accepted that increasing w/c ratio decreased the compressive strength due to the increase in the porosity. But, on the other hand, the presence of excess water ($w/c = 0.45$) lowered the curing temperature liberated during the hydration process resulting in improving the mechanical properties (Durtun, 1944). These two contradicting factors compensate each other and hence undetectable change in compressive strength values were attained. In presence of borate waste simulates, increasing the

water/cement ratio from 0.40 to 0.45 decreased the compressive strength of the final waste form. Beside the increase in porosity caused by excess water, the addition of borate salts to cement composite adds a new negative factor to that previously mentioned before. The presence of excess water favors the release of more borate ions (John et al., 1991) which retard the hydration process of cement resulting in lowering compressive strength values.

Experimentally it was found that mixing the cement with polymer increased the compressive strength values for the final waste form with $w/c = 35\%$ and containing 4% borate waste simulate from 167 kg/cm² for the cement final waste form to 250 kg/cm² for the final PE-cement composite waste form. This confirms that the proposed polyester improve the mechanical properties of the final waste forms. (Cook et al., 1994 & Granju and Maso 1984 & Granju and Maso, 1984 & Parcevaux, 1984).

X-ray diffraction of plain cement, polymer modified cement and solid waste form containing 4% borate waste simulate was performed to illustrate the effect of water/cement ratios and to confirm the previously obtained compressive strength data. Fig. (1) shows the effect of increasing w/c ratio from 0.35 to 0.5 on cured cement pastes (curves a, b), polyester modified cement (curves c, d) and polyester modified cement containing 4% borate simulate waste forms (curves e, f). The portlandite phase (CH) was identified at a d-value of 4.95 \AA , beside an appreciable amount of unavoidable carbonation forming calcium carbonate (Cc) at d 3.035 \AA of cement paste, the high sulphate form of calcium sulphaaluminate hydrate [ettringite (E)] is identified at d values, of 9.93 and 5.6 \AA . The remaining unhydrated cement clinkers were also identified at d values, of 2.77 and 2.74 \AA . Fig. (1)b shows that the amount of portlandite liberated was markedly less in high w/c ratio (0.50). Similar trend was observed in the literature (Su et al., 1991 and Ben-Dor et al., 1985). For PE modified cement waste forms the ettringite phase (E) was favored at higher w/c ratio (0.50), Fig. (1)f, while for lower w/c ratio (0.35) the monophase (the low sulphate form of calcium sulphaaluminate hydrate (Mo)) was predominant, Fig. (1)e.

It is worth mentioning that the presence of borate waste caused a noticeable retardation of the cement hydration and the portlandite phase (CH) under these conditions is weak (Ghattas et al., 1998 & Shatta, 1996). Also the addition of polyester to cement causes

reduction of portlandite liberated (CH), Fig. (1).

Porosity Measurements

Porosity and pore size distribution of polymer cement waste forms are considered as important parameters affecting both mechanical and chemical properties of the final waste forms.

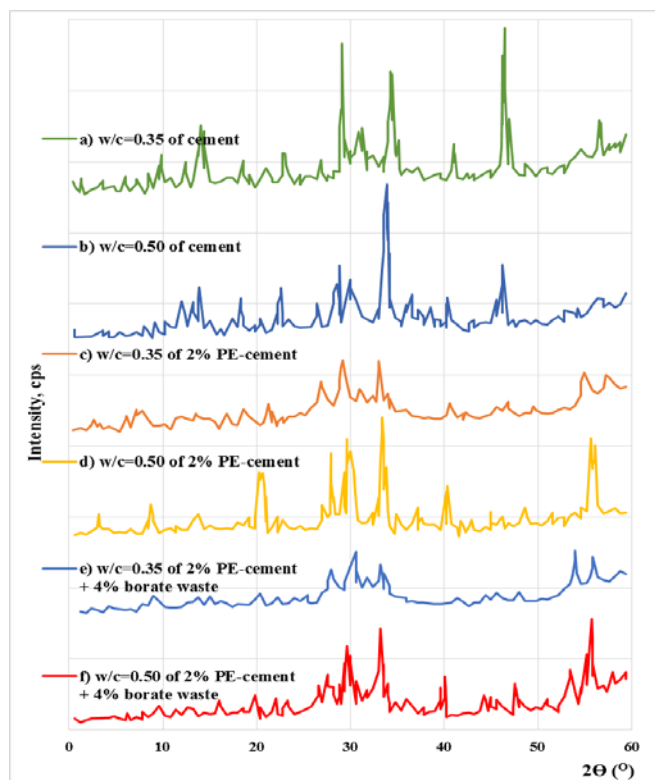


FIG. 1 X-RAY DIFFRACTOGRAMS OF PLAIN CEMENT, PE-CEMENT AND 2%PE-CEMENT CONTAINING 4% BORATE WASTE SIMULATE WITH DIFFERENT WATER/CEMENT RATIOS

Based on previous published work using PE modified cement, (Ghattas et al., 1998), porosity measurements were performed using 2 % by weight polyester with and without 4% by weight borate waste simulate.

Table (5) represents some porosity parameters namely total intrusion volume, medium pore diameter, average diameter, and percentage of porosity. From the obtained data it could be noticed that the presence of polyester reduces the porosity of cement. Borate waste reduces also the porosity of cement (Shatta, H.A. Ph.D., 1996). The addition of polymer reduces the pore diameter due to void reduction of cement pores, and consequently reduces the other porosity parameters.

Chemical Properties

Chemical stability of immobilized waste forms in aqueous media invariably assessed to avoid return of radionuclides from waste forms to the environment.

Leaching is generally considered as a basic criterion to evaluate the safety acceptability and chemical behavior of the final waste form in the disposal sites (Plecas et al., 1991).

In the present study we compared the polymer modified cement composite with plain cement matrix as inert chemical barriers. The chemical stability of immobilized waste forms in distilled and ground water were studied using radiocesium as a tracer.

TABLE 5 PORE SIZE DISTRIBUTION OF PLAIN CEMENT, AND PE-MODIFIED CEMENT WASTE FORMS WITH AND WITHOUT BORATE WASTE SIMULATE

Porosity parameters	Plain cement	Cement + 4% borate	2% PE premixed-cement	2% PE-premixed cement + 4% borate
Total intrusion volume (cc/g)	0.031	0.1663	0.0364	0.0507
Median pore diameter (μm)	0.2846	0.1242	0.1077	0.0546
Average penetration diameter (DV/A)	0.2823	0.0982	0.0929	0.0317
Porosity	39.23	36.225	36.7	34.569

(w/c = 0.35)

Leaching tests were performed according to Hepse's method (Hespe, 1971). The solid blocks, having similar dimensions to those used for mechanical tests, were hold in special containers, and the whole surface area of the specimen was exposed to leaching solution.

The effect of water/cement ratio (w/c) on the leachability of radiocaesium from polyester modified cement borate waste forms leached in ground water is shown in Fig. (2). For all samples studied, increasing w/c ratios increased the cumulative leach fraction due to the increase in porosity of the final waste forms (Seishi and Della 1981, Flumm et al., 1993).

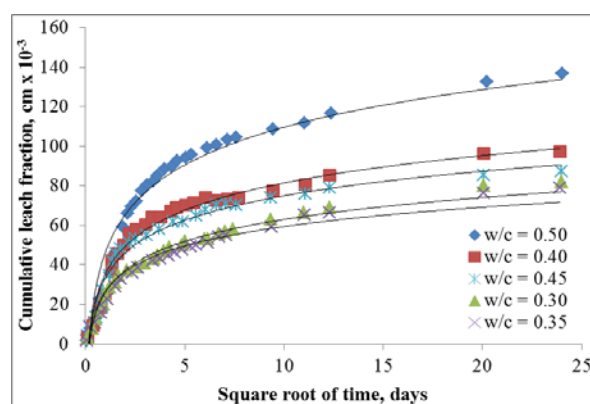


FIG. 2 CS-137 RELEASE FROM 1% PE-PREMIXED CEMENT WASTE FORMS IMMOBILIZING 4% BORATE WASTE HAVING DIFFERENT W/C RATIOS LEACHED IN GROUND WATER

The results shown in Fig. (3) indicated that the

cumulative leach fraction of Cs-137 from PE modified cement matrix immobilizing 4% by wt. borate waste simulate in case of using ground water as leachant is lower than that in case of distilled water for both w/c ratios (0.35 – 0.40). This may be due to the formation of an outer protective layer of insoluble compounds on the surface of solid blocks subjected to ground water as leachant solution (Bayoumi, 1990). The presence of cement materials in ground water leachant creates an alkaline medium with relative high pH value favorable for the fixation of different cations present in the ground water on the surface of the specimens studied (Bayoumi, 1990) which in turn lowered the porosity and hence showed low leachability.

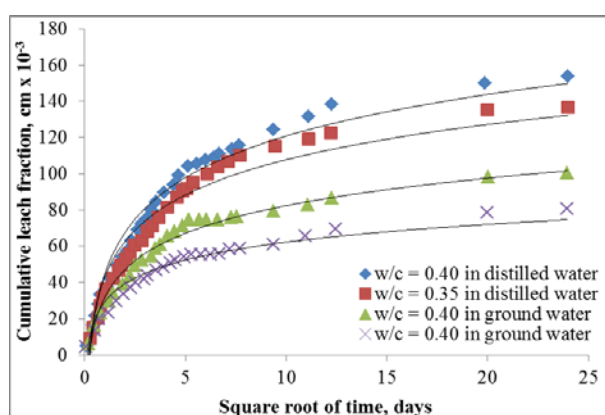


FIG. 3 THE RELEASE OF CS-137 FROM 1% PE-PREMIXED CEMENT WASTE FORMS IMMOBILIZING 4% SIMULATED BORATE WASTE IN DISTILLED AND GROUND WATER

The addition of 2% polyester decreased the cumulative leach fraction of cement borate waste forms, Fig. (4). This could be explained by the fact that the presence of polymer reduces the porosity of the waste form lowering the percolation of water through the samples. The results were in good agreement with the previous results of the porosity and mechanical properties of polyester modified cement waste forms (Ghattas et al., 1998).

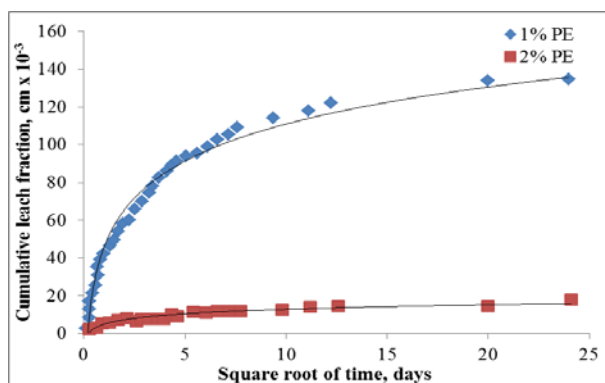


FIG. 4 THE RELEASE OF CS-137 FROM FINAL WASTE FORM CONTAINING TWO DIFFERENT POLYMER-CEMENT RATIOS

The leach coefficient (Lc) and leach index (Li) of radiocaesium from plain cement and polymer modified cement waste forms were calculated and the values obtained were found to be within the limits given in the literature for similar cement waste forms (McIsaac, 1993 and Walter and Serne, 1988).

Moreover, lower cumulative leach rate and higher leach indices were noticed for w/c ratio at 0.35, which recommended to be used for the preparation of the final waste forms. This is in agreement with the other properties of the waste forms namely the porosity and mechanical integrities.

It is worth mentioning that all leach indices which calculated for polymer modified cement waste forms were higher than 6, (Table 6). Furthermore, it is important to point out that all values of leach coefficients and leach indices obtained (for samples having w/c = 0.35) match very well with those values previously obtained for cumulative leach fractions.

TABLE 6 EFFECT OF DIFFERENT PERCENTAGE OF W/C ON LEACH INDEX (Li) AND LEACH COEFFICIENT (Lc) VALUES USING DISTILLED AND GROUND WATER (RADIOCESIUM WAS USED AS A TRACER)

W/c ratio	1% PE-cement waste forms using ground water	
	Lc	Li
0.30	5.03×10^{-7}	6.3
0.35	3.99×10^{-8}	7.4
0.40	4.9×10^{-7}	6.3
0.45	5.9×10^{-7}	6.2
0.50	1.0×10^{-6}	6.0
W/c ratio	1% PE-cement waste forms using distilled water	
	Lc	Li
0.35	1.5×10^{-7}	6.8
0.40	0.61×10^{-6}	6.21
W/c ratio	2% PE-cement waste forms using distilled water	
	Lc	Li
0.35	3.3×10^{-10}	9.5

Conclusions

According to mechanical measurement, porosity evaluation and X-ray diffraction analysis, it can be concluded that the proposed polymer modified cement matrices can be used as immobilization media for borate waste originating from pressurized water reactor and meet the criterion of the American Nuclear Regulatory.

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